

# **AIR QUALITY IMPACTS OF ETHANOL IN CALIFORNIA GASOLINE**

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Numerous analyses have been done demonstrating the ozone equivalency of gasolines blended at roughly the same volume of either ethanol or MTBE. While ethanol blends might lead to greater evaporative emissions than MTBE, the ethanol-related emissions can be lower in reactivity and will provide greater carbon monoxide reductions. Unfortunately, these are benefits that are fully appreciated only when assessing how ozone is ultimately formed in the atmosphere (such as in urban airshed modeling studies). These benefits are not easily recognized when comparing just vehicle emissions. This “White Paper” provides a framework for reconciling the increased emissions resulting from ethanol blended gasolines with the lower reactivity and carbon monoxide emissions effects ethanol will have in the atmosphere. The analyses presented here show that a significant offset for ethanol's increased evaporative emissions can be found in it's increased oxygen content and reduced reactivity. In fact, the differences in ozone forming potential of ethanol and MTBE generally are seen to be small relative to existing standards.

## **Background**

Ethanol is an alternative oxygenate to MTBE for use in California Cleaner Burning Gasoline (CBG), but it has some properties that are different from MTBE. From the standpoint of octane and driveability properties, similar volumes of ethanol could be used interchangeably in the existing CBG program other than the need for terminal blending. However, such ethanol blends would have nearly twice the fuel-oxygen content of the MTBE blends, and these ethanol blends could have as much as a 1 psi higher (Reid vapor pressure) RVP volatility unless the base clear-gasolines were pre-adjusted to accommodate this volatility property of ethanol. If the volatility were fully adjusted, tests have shown that the extra oxygen in the ethanol can reduce exhaust emissions of carbon monoxide (CO) and volatile organic compounds (VOC), especially for higher emitting vehicles. That is, switching to ethanol (at essentially equal volume) with a volatility adjustment could improve air quality compared to the present utilization of MTBE. Likewise, there appears to be some level of volatility pre-adjustment for using ethanol that would achieve some form of air quality equivalence to MTBE in the existing CBG program.

Estimation of a volatility adjustment where oxygen-related exhaust reductions neutralize volatility increases can be very complicated. Any air quality “neutrality” between ethanol and MTBE must also be defined through averages in time and space, because local impacts will vary due to non-linear and multiple-precursor effects. The California CBG program is directed

mainly at photochemical smog abatement focusing on the VOC and NO<sub>x</sub> precursors, but smog formation involves many precursor categories that are not equally affected between fuel oxygen and volatility. Moreover, CO is a recognized precursor to urban ozone (or smog) that appears to be growing in importance relative to VOC. For example, the newest California LEV II regulations allow CO-to-VOC emissions ratios of up to 100-to-1 even though the ozone-forming potential of CO is only about 50-to-1 relative to exhaust VOC. As a consequence of such emissions ratios, the carbon monoxide from such vehicles can generate more urban ozone than their exhaust VOC emissions.

The U.S. EPA and the California Air Resources Board (ARB) currently list many sources (or separate categories) of vehicle emissions: exhaust (from the tailpipe), refueling (from spillage and vapors), resting losses (primarily seepage from the fuel system), running losses (other than the tailpipe), diurnal (primarily vapors released due to daily changes in ambient temperature), and hot soak (primarily vapors released after driving). Some of these non-exhaust sources like spillage and seepage are minimally affected by volatility. Each of these different sources are estimated by the U.S. EPA using a computer model called MOBILE, the ARB model is EMFAC. The ARB further divides exhaust emissions into starting and running parts. Each of these emissions categories can respond differently to either the oxygen or the volatility differences between ethanol and MTBE. Moreover, the spectrum of VOC's associated with each vehicle emissions source are not only different for each gasoline, the responses to ethanol and MTBE can also vary. Moreover, the response to changes in fuel composition for both the mass and the VOC spectrum of each source can depend on parameters such as control technology, maintenance, tampering, temperature, and speed. For example, VOC's from the tailpipe contain intermediate combustion products such as olefins and aldehydes not found in the original fuel, plus some unburned gasoline itself, all of which have been further modified (i.e., reduced or altered in varying amounts by the catalyst in the individual onboard emissions control system).

Evaporative (or the sum of the five non-exhaust) emissions will have virtually no combustion-related VOC (or CO or NO<sub>x</sub> either), so the non-exhaust VOC emissions will depend heavily on the fuel composition and volatility characteristics. Since the various non-exhaust emissions occur over different temperature ranges (e.g., refueling emissions from relatively cool gasoline that had be stored underground versus hot soak emissions after a drive), the distillation-like effects of fuel volatility will release different groups of molecules depending on their individual boiling points and vapor pressure effects.

Fuel volatility is most often characterized by Reid vapor pressure (RVP), the pressure in pounds per square inch (psi) of gasoline at a temperature of 100 °F. Adding a low boiling (highly volatile) molecule like isopentane will raise RVP, while making gasoline with less isopentane or other highly volatile molecules will reduce RVP. What makes the various temperature characteristics of non-exhaust emissions and the volatility characteristics of gasoline so important is the fact that the highly volatile components like butane and other light

paraffins are generally much less photochemically reactive towards ozone formation than the low-volatility heavy components of gasoline like xylenes and tri-methyl benzenes.

The exhaust emissions are CO, NO<sub>x</sub> and a complex mixture of different VOC, but it is important to note that exhaust VOC mixtures as a whole are more photochemically reactive (on a per unit weight basis) towards ozone formation than are any non-exhaust VOC emissions categories. Non-exhaust emissions nevertheless, can still vary in reactivity as fuels are adjusted for RVP or as the local temperatures and driving characteristics (e.g., speed and number of hot soaks) vary. The total mass of exhaust emissions and the total mass of non-exhaust emissions are each also subject to separate control regulations, driving characteristics and fuel formulations.

### **Why Vehicle Mass Emissions Differ from Using Ethanol Blends Instead of MTBE Gasoline**

The presence of oxygen in the fuel tends to raise the effective air-to-fuel ratio for combustion. There may also be a special impact from fuel oxygen on catalyst efficiency because studies have shown greater reductions of CO and VOC at the tailpipe than in the exhaust manifold (see SAE Paper No. 920329). Emissions of carbon monoxide and volatile organic compounds typically decrease while NO<sub>x</sub> emissions sometimes increase as the air-to-fuel ratio increases. NO<sub>x</sub> emissions are more complicated because they may actually be more related to the type and state of the emissions control system (See SAE Paper No. 950812) than to the net combustion temperature. Also the combustion temperature of fuel components like ethanol have a lower combustion temperature than the hydrocarbons in gasoline. While the oxygen in ethanol can raise the air-to-fuel ratio which may increase combustion temperature, the lower temperature of combustion for ethanol mitigates this effect. Also the dilution and octane equivalent effects further complicate the net combustion temperatures that may affect NO<sub>x</sub> emissions.

Although the newest emissions control systems have oxygen sensors in the tailpipe to adjust the air-to-fuel ratio, part of the cold start phase and some heavy acceleration conditions may not be controlled by these oxygen sensors. Both the cold start phase and heavy acceleration are periods of high emissions. Hence, the oxygen in ethanol can be expected to reduce CO and VOC emissions during these high-emissions conditions in new vehicles and during all conditions for vehicles that do not have operational oxygen sensors or catalysts.

The chemical combustion effects are also interrelated to the physical volatility effects through the on-board equipment designed to control evaporative emissions of VOC. A key component of this equipment is a canister which absorbs VOC vapors associated with the fuel system. The canister is purged into the engine when a vacuum exists in the intake manifold. The VOC which are then desorbed during purging add to the fuel coming from the fuel injectors (or carburetors) to lower the air-to-fuel ratio that enter the combustion chamber. Fuel of higher volatility will add more VOC loading to the canister and, hence, tend to reduce the air-to-fuel

mixture (especially when the oxygen sensor is not operating) more than a fuel of lower volatility. Computer controls, such as adaptive learning, on the newest vehicles can mitigate this effect by sensing the temperature when the engine was turned off and the temperature when the engine is restarted to estimate the cold start requirements for fuel until the oxygen sensor takes over. That is, the fuel from the injectors can be reduced so that the VOC from the canister won't drive the air-to-fuel ratio so low that CO and VOC exhaust emissions might be increased.

### **Using the UAM to Assess the Impact of Ethanol**

Under the Clean Air Act Amendments (CAAA) of 1990, areas with serious ozone problems, like California, are required to demonstrate attainment of the national ozone standard and "This attainment demonstration must be based on photochemical grid modeling." The Urban Airshed Model (UAM) is recognized by both the U.S. EPA and the California Air Resources Board (ARB) as a photochemical grid model recommended for use in satisfying the CAAA requirement and for assessing the ozone impacts of changes in major emissions sources like motor vehicles. For example, the ARB recently used UAM modeling results to grant VOC equivalency to the use of radiators coated with an Engelhard catalyst that removes ozone. Therefore, the UAM is a proper tool to assess the ozone equivalency of using ethanol in place of MTBE in California Cleaner Burning Gasoline (CBG).

Several sensitivity simulations have been performed using the UAM for this ethanol evaluation. As a rule each of these simulations tested the impact of each mobile emissions category by eliminating it from the UAM emissions input. Results from this set of sensitivity scenarios can then be combined using alternative assumptions to predict the results of ethanol scenarios.

The base simulation comes from the 1997 Air Quality Management Plan (AQMP) available on the internet at <http://www.aqmd.gov/aqmp/97aqmp>. The main information on the use of the UAM in the AQMP can be found in Appendix 5, Chapter 3 of the AQMP documentation. The simulations reported here use the same input files (or input file preparation software) as were used in the AQMP for the control simulations for the year 2000 based on the meteorological episode on the 27<sup>th</sup> and 28<sup>th</sup> of August 1987.

Besides providing information useful to evaluating the use of ethanol, these sensitivity simulations illustrate the relative importance of the various parts of the gasoline-related mobile emissions inventory. For the most part these simulation scenarios involve setting a particular part of the gasoline-related inventory to zero. For carbon monoxide (CO), two sensitivity simulations were performed to bracket the impact of gasoline-related CO emissions. For one CO scenario the chemistry of CO was totally eliminated and for the other the gasoline-related emissions were set to zero. The former includes non-gasoline related emissions, secondary CO from VOC, carry-over from previous days, plus initial and boundary conditions. The latter involves only gasoline-related emissions. The actual impact of such emissions would be expected

to fall somewhere between these simulations because the emissions would affect initial and boundary conditions over a period of several days due to the month-long atmospheric lifetime of CO compared to the day-long lifetimes of urban VOC.

A potential update to the AQMP is included as a sensitivity scenario that uses a newer running-exhaust profile (#882) supplied by P. Allen of the ARB. The original AQMP profile had 57 percent methane; the new profile has 18 percent methane, and for reference the Caldecott tunnel data show 9.9 percent methane. The newer profile (#882) resulted from a special ARB workshop this past summer.

The results of the UAM sensitivity runs are given in Tables 1 and 2. No 8-hour results were part of the AQMP, but they are included here to be used as a guide for potential impacts to the new ozone standard<sup>1</sup>. All results in Table 1 come from the highest simulated concentration in the UAM for each day. Impacts are given for single cells and in general such cells do not correspond to the cells that have the highest total ozone concentration. To obtain impacts at the highest ozone concentration one must subtract the appropriate base case value shown; for convenience Table 3 presents the impacts for the 28 August day peak concentrations.

Table 1. 1-Hour Maximum Ozone (ppb) Results of UAM Simulations.

Scenario	August 27 <sup>th</sup>	Highest Impact	Lowest Impact	August 28 <sup>th</sup>	Highest Impact	Lowest Impact
Base	129.0			148.3		
+15%NO <sub>x</sub>	125.7	+2.2	-6.3	148.8	+2.5	-11.9
CO Chem	114.1	-0.1	-16.1	132.4	-0.2	-33.3
CO Emiss.	126.4	+0.7	-4.5	143.3	+0.5	-9.1
Run Evap	127.8	+0.2	-4.2	146.9	+0.3	-4.8
Hot Soak	128.1	+0.1	-2.0	147.7	+0.2	-3.1
Diurnal	125.4	+1.3	-7.7	145.4	+1.2	-7.4
VOC Strt	121.6	+1.3	-12.6	143.9	+1.0	-22.8
VOC Rn	125.3	+0.5	-6.2	144.7	+0.4	-11.9
Rn Spec.	132.0	+5.5	-0.3	150.9	+10.6	-0.4

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<sup>1</sup> Because some concern has been expressed over the use of the standard UAM-IV for 8-hour ozone concentrations that include darkness, the 8-hour period between noon and 8 pm PDT has been used here. Comparisons with maximum values at any hour show that for the 28 August day there are very small differences. A more recent version of the UAM (UAM-V as used in OTAG) includes a special layer at ground level and improved surface effects that combine to enhance the accuracy of simulated ozone concentrations during darkness.

Table 2. 8-Hour Maximum Ozone (ppb) Results of UAM Simulations. Because there have been questions about the UAM-IV evening ozone values, the 8-hour values used here are all noon to 1800 PDT.

Scenario	August 27 <sup>th</sup>	Highest Impact	Lowest Impact	August 28 <sup>th</sup>	Highest Impact	Lowest Impact
Base	93.6			132.1		
+15%NO <sub>x</sub>	93.6	+1.6	-5.5	131.1	+1.6	-8.6
CO Chem	86.1	-0.1	-11.7	117.4	-0.2	-20.6
CO Emiss	92.3	+0.3	-3.1	127.7	+0.3	-6.1
Run Evap	93.2	+0.4	-3.2	130.6	+0.1	-3.3
Hot Soak	93.3	+0.1	-1.2	131.3	+0.1	-2.4
Diurnal	92.5	+0.9	-4.1	129.3	+0.4	-4.8
VOC Strt	92.2	+0.5	-8.3	127.0	+0.7	-16.4
VOC Rn	92.6	+0.3	-4.7	128.1	+0.3	-9.2
Rn Spec.	95.8	+3.9	-0.3	135.0	+7.6	-0.2

Table 3. The important peak impacts for the 28 August day to be used in the ethanol assessment. These are obtained in each case by subtracting the appropriate base simulation values (148.3 ppb for the 1-hour and 132.1 ppb for the 8-hour, respectively) shown in Tables 1 and 2.

Scenario	August 28 <sup>th</sup> 1-hour	August 28 <sup>th</sup> 8-hour
+15%NO <sub>x</sub>	+0.5	-1.0
CO Chem	-15.9 (-9.5 for 60%)	-14.7 (-8.8 for 60%)
CO Emiss	-5.0	-4.4
Run Evap	-1.4	-1.5
Hot Soak	-0.6	-0.8
Diurnal	-2.9	-2.8
VOC Strt	-4.4	-5.1
VOC Rn	-3.6	-4.0
Rn Spec.	+2.6	+2.9

## Ethanol Impacts

Using the results from Table 3 and various assumptions about substituting ethanol for MTBE in CBG one can estimate the net impacts on ozone predicted for a UAM simulation that might actually use the same set of assumptions. It should be noted before combining the UAM results that gasoline-related CO emissions are only 60 percent of the total CO emissions as seen in the AQMP emissions inventory.

Using the VOC and mobile CO impacts (and the new profile) the entire combined gasoline-related mobile contribution to peak impacts on the August 28 day are 20.5-25.0 and 21.5-25.9 ppb, for the 1-hour and 8-hour peaks, respectively. The ranges shown here are due to the bracketing of the CO impacts. Although the tables indicate that changes in NO<sub>x</sub> of up to 15 percent of the gasoline-related fleet show mixed and fairly small impacts, the entire fleet NO<sub>x</sub> impact is considered to be too severe and non-linear to be included here.

The exhaust impact of using ethanol in place of MTBE can be estimated using the Predictive Model. The Predictive Model is based on over 7000 data points from a wide range of fuel effects covering a broad range of model-year and emissions levels. The new ARB test data, although directed at the MTBE to ethanol substitution, in reality provide only 24 new data points to the existing 7000 data-point base on the mass emissions impacts related to changing fuel parameters. Moreover, the new data relate only to low-emitting vehicles in the 1990-1995 model-year range. The Predictive Model database contains earlier model-year information and some higher-emitting vehicles. The 12-vehicle fleet in the new ARB data has been estimated to represent less than 10 percent of the overall 1998 mobile VOC emissions. However, the ethanol and MTBE fuels used in the new 12-vehicle tests can be representative of substituting ethanol for MTBE in CBG on a volume basis.

Using the specifications of the two fuels in ARB 12-vehicle tests, the California Predictive Model indicates a 3.2 reduction in exhaust organic emissions. It should be noted that a regression analyses by SAI indicates that the oxygen impact in the Predictive Model may be under-represented due to the lack of a separate statistical treatment for above-normal (i.e. above 400 mg/mi) emitting vehicles. That is, the 3.2 percent reduction seen in the existing Predictive Model may under-predict the ethanol impact that could be supported by the same 7000 data-point database.

An accepted credit for CO reduction due to oxygen is 5 percent per percent fuel oxygen (see *Interagency Assessment of Oxygenated Fuels*, Office of Science and Technology Policy, 1997). This is half the impact seen in the Caldecott Tunnel data published by Kirchstetter et al. in 1996 (*Environmental Science & Technology*, Vol. 30, pages 661-670). Since the ARB's analysis of the ethanol blend showed 3.94 percent oxygen compared to only 2.09 in the MTBE, the

ethanol CO reduction credit would be [5 times (3.94 – 2.09)] 9.25 percent. The ARB analysis of the new 12-vehicle data shows a similar impact of 10 percent.

The ARB recently distributed an evaporative model during the CBG “flexibility” workshops this past year. This model indicates that the three parts of evaporative emissions increase by the following percentages for a 1 psi RVP increase from 7 psi: for diurnal the increase predicted is 26.6 percent, for hot soak the model predicts a 51.7 percent increase, and for running losses it predicts an increase of 45.7 percent. Also a statistically significant 30 percent reactivity credit for ethanol in hot soak was observed in the six vehicles tested recently by the ARB.

Additionally, the AQMP and the ARB use identical reactivity profiles for hot soak and running losses, so the 30 percent credit for ethanol could presumably be applied to running loss emissions as well.

Table 4. Mass impacts due to use of 10 percent ethanol in place of 11 percent MTBE with same CBG-ready base gasoline.

Source Category	Net Mass Impact	Source
Carbon Monoxide	-9.25	OSTP report plus others
Run Evap VOC	+45.7 (+2.0)	Evap model (with 30% MIR credit)
Hot Soak VOC	+51.7 (+6.2)	Evap model (with 30% MIR credit)
Diurnal VOC	+26.6	Evap model
VOC Strt	-3.2	Predictive Model
VOC Rn	-3.2	Predictive Model
Rn Spec.	-3.2	Predictive Model

The mass impacts are presented in Table 4 and can be summarized as follows: for exhaust VOC the Predictive Model gives a 3.2 percent reduction, for CO a 9.25 percent reduction, for diurnal a 26.6 percent increase, for hot soak a 51.7 percent increase, and for running losses a 45.7 percent increase. Reactivity credits include 30 percent each for hot soak and running losses. These mass impacts can then be combined using the values shown in Table 3.

The initial results indicate that a 1 psi waiver might increase ozone by 0.5-0.9 ppb and by 0.6-1.0 for the 1-hour and 8-hour peaks, respectively, for a August 28 AQMP simulation. Since the total fleet VOC and CO impacts are 20.5-25.0 and 21.5-25.9 ppb for the 1- and 8-hour peaks, these ethanol impacts are estimated to be about 2-5 percent of the ozone attributable to gasoline-related VOC and CO sources.

If the hot soak (and running losses) reactivity credit shown in the ARB tests is taken, then the impacts become –0.4 to zero ppb for either the 1-hour or the 8-hour peaks. That is, the full 1

psi waiver would be justified. If instead of a reactivity credit the waiver were reduced to 0.6 psi, then the results might also be interpreted to show essentially equal ozone between the MTBE and ethanol blend. If some extra credit were given for higher emitting vehicles (but not the observed evaporative reactivity credit), a waiver closer to a full 1 psi might also be simulated. For example, if the exhaust VOC reduction for ethanol were increased from the Predictive Model value of 3.2 percent to about 4.5 percent with higher emitters, and the CO reduction of 9.25 percent estimated above were increased to 12 percent, then a waiver near 0.8 psi might be justified.